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PROVISIONAL APPLICATION COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 C.F.R. § 1.53(c).

TITLE: POLYMER STABILIZED METAL, ALLOY, AND SEMICONDUCTOR
NANOPARTICLES FOR CATALYTIC REACTIONS IN SUPERCRITICAL
CARBON DIOXIDE

Inventor(s)/Applicant(s): Chien M. Wai, Hiroyuki Ohde and Mariko Ohde

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- ☒ 29 pages of specification are enclosed.
- ☒ Small entity status is claimed for this application.
- ☒ Provisional Filing Fee Amount:
☒ \$ 80, small entity
- ☒ A check in the amount of \$80.00 to cover the filing fee is enclosed.
- ☒ The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. The name of the U.S. Government agency and the Government contract number are:
1. NSF contact No. is (Idaho NSF-EPSCoR (EPS-0132626))
2. ARO contact No. is (Army DEPSCoR DAAD19-01-1-0458).

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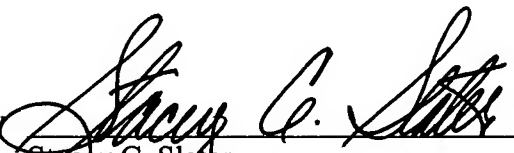
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Potential Applications of the “Polymer Stabilized Metal, Alloy, and Semiconductor Nanoparticles for Catalytic Reactions in Supercritical Carbon Dioxide”

1. Hydrogenation of arenes: converting toxic aromatic compounds such as benzene to harmless cyclohexane. Applications: (1) reduce benzene contents of diesel fuels, (2) aromatic hydrogen storage systems for fuel cell applications (e.g. cyclohexane can release 3 moles of hydrogen gas for fuel cell reactions. Benzene becomes cyclohexane in this process which can be charged with hydrogen by nanoparticle catalyzed hydrogenation in supercritical CO₂ to regenerate cyclohexane).
2. Hydrogenation of olefins: converting C=C double bonds to C-C single bonds for various organic syntheses. One potential application is the synthesis of chiral compounds. If the matrix polymer is chiral, hydrogenation of a prochiral olefin in supercritical CO₂ may end up with a chiral product. It may have applications for drug synthesis. Chiral polymers can be synthesized from chiral monomers. Since most of natural polymers consist of chiral monomers, these polymers may be used for supporting metal nanoparticles for chiral syntheses.
3. Hydrodechlorination of chlorinated compounds: Toxic chlorinated compounds including PCBs can be converted to harmless compounds by catalytic hydrogenation in supercritical CO₂ using the polymer stabilized nanoparticles.
4. Converting nitro groups to amines: Catalytic hydrogenation in supercritical CO₂ can convert nitro groups in organic compounds to amines. This may be a method for disposal of explosives containing nitro groups.
5. Fuel cell membrane preparation: Polymer films containing metal nanoparticles are used as membranes for fuel cell applications. Our supercritical fluid technology for depositing metal nanoparticles in polymer materials may provide a method of making catalytic membranes for fuel cell applications.
6. Environmental remediation with TiO₂ nanoparticle photocatalytic reaction : TiO₂ can reduce oxygen by absorption of photo energy to form superoxide anion (O₂⁻) which decompose organic compounds include bacteria. It is well known that the catalytic activity of semiconductor photocatalysts increases as the size of semiconductor particle decreases in nanometer range. Optically transparent plastic materials may be used for this application in a supercritical CO₂ solution.

**Hydrodechlorination in Supercritical CO₂ Catalyzed by
Pd and Rh Nanoparticles Stabilized in Plastics**

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Hydrodechlorination catalyzed by noble metals such as palladium and rhodium is one method of removing chlorine atoms from toxic chlorinated compounds^[1-3]. Catalytic activity, recyclability and easy separation of products from the catalyst are considered three important criteria to evaluate the performance of the noble metal catalysts. The high catalytic activities of nanometer-sized noble metal particles reported recently in the literature appear promising for many industrial and environmental applications^[4,5]. A number of methods for preparation of metal nanoparticles are known in the literature^[6-9]. Since metal nanoparticles are generally unstable, exploration of appropriate supports for stabilizing the metal nanoparticles is a key factor for their successful applications in catalysis.

In the present work, we have stabilized Pd and Rh nanoparticles in supercritical CO₂ using commercially available plastic granules and tubes as supports. The stabilization is based on the fact that plastics swell in supercritical CO₂^[10,11] allowing the fluid phase to penetrate and disperse metal precursors inside the whole plastic material. After chemical reduction of metal precursors, nanometer-sized metal particles are formed and trapped in fine structures of the plastic matrix preventing their agglomeration. During catalytic reactions using the plastic stabilized metal

nanoparticles in supercritical CO₂, the plastic swells again allowing reactants dissolved in the fluid phase to diffuse into the interior of the plastic material contacting all of the nanoparticles stabilized in the plastics. The metal nanoparticles are still trapped in the plastic structures during catalytic reactions, because of much larger hydrodynamic radius of the nanoparticles relative to the reactants (hydrogen and chlorinated benzenes). Thus, catalytic reactions are not limited to metal nanoparticles deposited on the plastic surface but involve all nanoparticles trapped inside the plastics. As a result, greater catalytic efficiencies are obtained using these plastic stabilized metal nanoparticles for catalysis in supercritical CO₂ and the catalysts can be reused.

This communication describes our experimental procedures and initial results of Pd and Rh nanoparticles catalyzed hydrodechlorination of several chlorobenzenes and a chlorobiphenyl in supercritical CO₂. Some attractive features of this dechlorination method are that the products can be separated from the catalyst by a simple expansion process and that the catalysts can be repeatedly used with little change in catalytic capability. Benzene and biphenyl with one chlorine substitution are used as testing compounds because removing the sole chlorine atom from benzene and from biphenyl is known to be more difficult than that from polychlorinated biphenyls.






The Pd and Rh nanoparticles were deposited into two types of commercial plastics granules and tubes in supercritical CO₂. One type was high density polyethylene (HDPE) granule with 3 mm size obtained from Goodfellow (Berwyn, PA). Another type was perfluoroalkyl-tetrafluoroethylene copolymer (PFA) tubes with 6 mm diameter obtained from Fisher (Pittsburgh, PA). The PFA tube was sliced to rings with 1 mm width for metal deposition experiments. The plastic materials were placed in a 50 mL volume stainless steel vessel together with 250 mg of a metal precursor. Palladium (II) hexafluoroacetylacetonate, Pd(hfa)₂, and rhodium (III) acetylacetonate, Rh(acac)₃, were used as precursors for Pd and Rh nanoparticles, respectively. The 50 mL cell was preheated to a deposition temperature (e.g. 50 °C for Pd) in an oven. After reaching the

desired temperature, neat CO₂ at 80 atm was introduced into the 50 mL cell to dissolve the Pd or Rh precursor. An injection vessel (10 mL volume), connected with the 50 mL cell by 1/16" tubing with an interconnecting valve, was pressurized with 10 atm hydrogen. After that, the injection vessel was pressurized by neat CO₂ to a total pressure of 200 atm. By opening the interconnecting valve between the 50 mL high-pressure cell and the 10 mL injection vessel, the CO₂-H₂ mixture was injected into the 50 mL high-pressure cell by the pressure difference. The hydrogen reduction of Pd(hfa)₂ was performed at 200 atm and 50 °C. The reduction and metal deposition process required about 3 hours. After the deposition, the color of the Pd-deposited PFA was dark gray from surface to the interior indicative of uniform distribution of the metal nanoparticles in the plastic materials. For deposition of Rh nanoparticles, 250 mg of Rh(acac)₃ was dissolved in 3.5 mL of chloroform together with 10 mg of Pd(hfa)₂. The Pd(II) complex was added to serve as a catalyst for hydrogen reduction of Rh in supercritical CO₂. The deposition of Rh into HDPE was performed at 110 °C with 10 atm of H₂ in 200 atm of CO₂. Figure 1a shows an optical image of HDPE granules with Rh(acac)₃ or Rh nanoparticles. As seen in the image, the orange color caused by Rh(acac)₃ changed to blackish indicative of formation of Rh nanoparticles. A TEM micrograph of a microtomed Rh-deposited HDPE (Figure 1b) reveals that the diameters of the deposited Rh nanoparticles vary from 2 to 10 nm with the largest fraction in the range of 4-5 nm. For deposition of Rh nanoparticles in PFA, the same conditions were used except the temperature was increased to 150 °C. The Pd and Rh nanoparticles stabilized in these plastics were stable in air and no obvious aggregation of the metal nanoparticles was observed based on TEM micrographs after storage in our lab for 3 months.

For the dechlorination experiments, the plastic catalysts were placed in a stainless steel chamber (10 mL volume) together with a chlorinated benzene. After closing the

reaction cell, hydrogen gas was flowed through the whole system to purge ambient air and then the cell was pressurized to 10 atm with hydrogen. After the stainless cell was heated to 50 °C in an oven, 100 atm of CO₂ was introduced into the cell for hydrodechlorination to take place. The results of hydrodechlorinations catalyzed by Pd and Rh nanoparticles stabilized in HDPE and PFA (Pd-HDPE, Pd-PFA and Rh-PFA) are given in Table 1.

Table 1 : Dechlorination of chlorinated benzenes using plastic stabilized Pd or Rh nanoparticles.

Chlorinated benzenes	Catalyst	Time (min.)					
<i>p</i>-chlorophenol	Pd-PFA	15	72	14	7	7	0
15 mg (1.2 x 10 ⁻⁴ mol)	Pd-HDPE	30	83	16	1	0	0
chlorobenzene	Pd-PFA	30	0	0	43	0	57
15 µL (1.5 x 10 ⁻⁴ mol)		60	0	0	85	0	15
2,4-dichlorophenol	Pd-PFA	70	40	48	9	0	0
15 mg (0.9 x 10 ⁻⁴ mol)	Rh-PFA	60	7	19	15	0	0

Pd nanoparticles stabilized in both HDPE and PFA were effective for removing chlorine from *p*-chlorophenol. With 10 atm of H₂ in supercritical CO₂, hydrodechlorination of *p*-chlorophenol was virtually complete in 15 or 30 minutes using Pd-PFA or Pd-HDPE as the catalyst, respectively. The main products were cyclohexanone and cyclohexanol for both catalysts. Removing chlorine from chlorobenzene was more difficult than from *p*-chlorophenol using the Pd-PFA catalysts. The dechlorination of chlorobenzene was complete within 30 minutes in supercritical CO₂ at 50 °C and 100 atm. Hydrogenation of benzene to cyclohexane was also observed after the dechlorination was completed. Dechlorination of 2,4-dichlorophenol with Pd-PFA was also studied, and the results are shown in Figure 2. The amount of

2,4-dichlorophenol decreased linearly with time and virtually disappeared at 70 minutes. The major products were cyclohexanol and cyclohexanone. The conversion of cyclohexanone reached 30 % at the first 30 minutes and didn't increase very much at extended reaction times. On the other hand, the conversion of cyclohexanol was very small (less than 10 %) at the first 20 minutes and almost linearly increased after that. The conversion profile of these two compounds may suggest a mechanism that 2,4-dichlorophenol was hydrogenated to cyclohexanol through formation of cyclohexanone. Rh nanoparticles are very effective for catalytic hydrogenations of olefins and arenes^[12]. The hydrodechlorination of 2,4-dichlorophenol was carried out using Rh-PFA, but the dechlorination rate was slower than that observed using Pd-PFA.

The plastic catalyst was used repeatedly to examine the recyclability. According to our experiments, if the catalyst was cleaned with neat CO₂ immediately after use, it could be reused for at least 10 times with negligible change in catalytic activity.

Hydrodechlorination of 4-chlorobiphenyl (BZ# 3) catalyzed by Pd-PFA was carried out using a different reactor system which consists of two stainless vessels, one is 15 mL volume reactor with the Pd catalysts and another is 40 mL volume vessel for storage of reactant (10 mg of 4-chlorobiphenyl). Hydrogen was flowed through both of the stainless chambers to purge ambient air first and then was pressurized to 10 atm. Since the solubility of 4-chlorobiphenyl increased at temperatures above its melting point (76-77 °C), the stainless vessels were heated to 80 °C in an oven. After reaching at 80 °C, CO₂ at 150 atm was introduced into the storage vessel to dissolve the 4-chlorobiphenyl and hydrogen. The CO₂ containing 4-chlorobiphenyl and hydrogen was then injected into the reactor by opening an interconnecting valve between the reactor and the storage vessel. The reaction products were collected in a CDCl₃ solution after 30 minutes of reaction time. The injection and collection processes were repeated continuously for 5 times to introduce all of the 4-chlorobiphenyl into the reactor for hydrodechlorination. Based on the NMR spectrum of the products collected in the CDCl₃ solution, it was found that 4-chlorobiphenyl passed through the reactor was

successfully dechlorinated (> 99 %) and that the products were 85 % of dicyclohexyl, 14 % of cyclohexyl benzene and < 1 % biphenyl. The NMR spectrum showed a H₂O peak besides the three products described above. The water was contained in the chlorobiphenyl reagent as impurity.

In the present work, we have demonstrated that chlorinated benzenes with one or two chlorine substituents and 4-chlorobiphenyl can be dechlorinated by hydrogen in supercritical CO₂ using plastic stabilized Pd or Rh nanoparticles as a catalyst. This efficient and clean catalytic hydrodechlorination method using supercritical CO₂ as a medium may have a wide range of applications in industrial and environmental processes. Further research along this direction is currently in progress.

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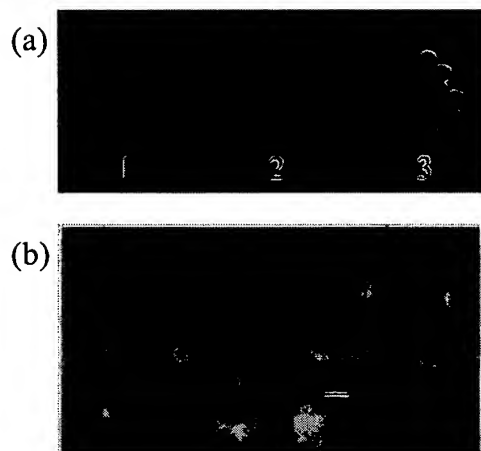


Figure 1 (a) Optical image of HDPE granules, 1) original, 2) with $\text{Rh}(\text{acac})_3$, 3) with Rh nanoparticles (b) TEM micrograph of Rh nanoparticles deposited in HDPE granule, scale = 20 nm.

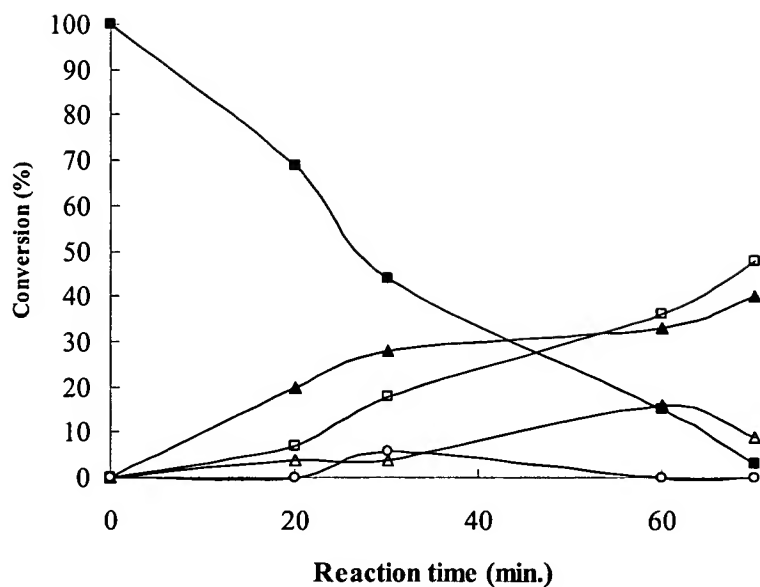
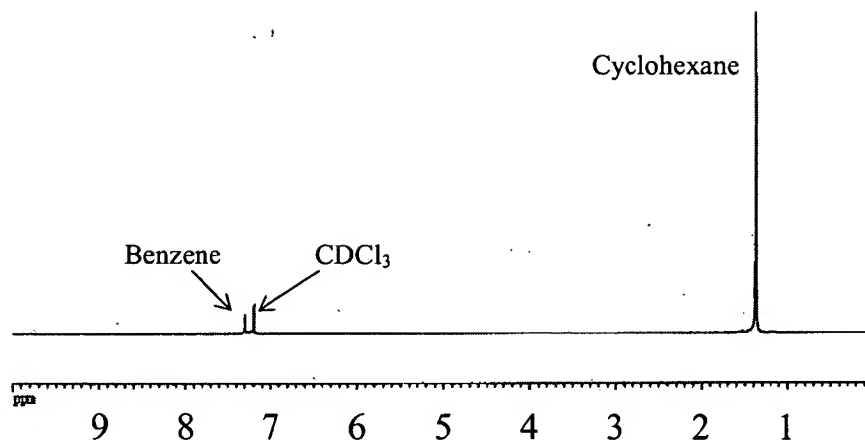
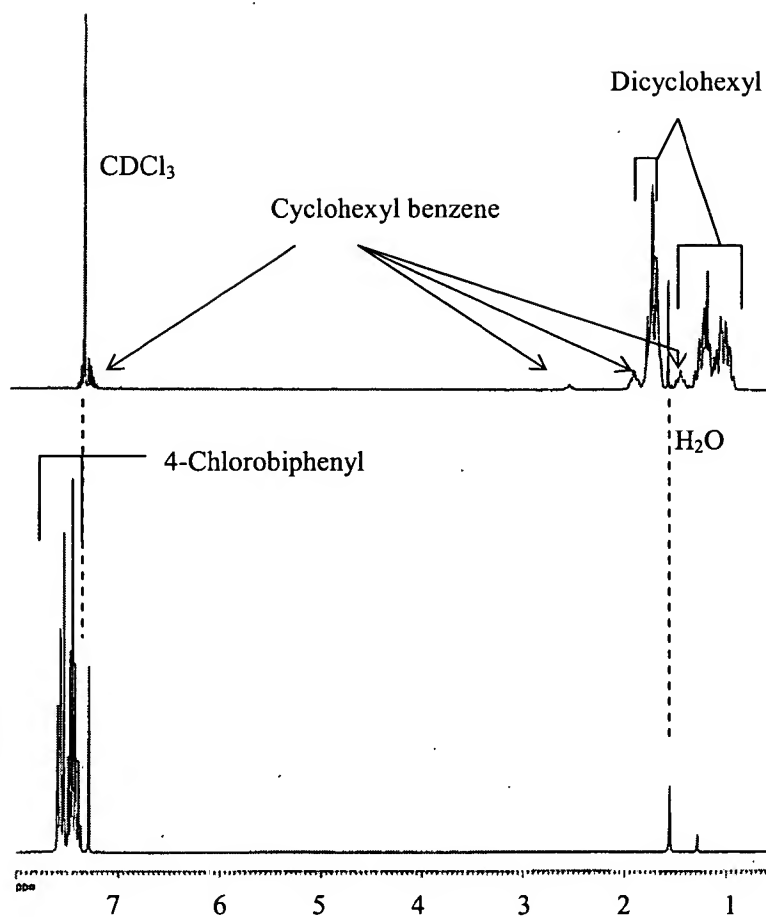


Figure 2. Hydrodechlorination of 2,4-dichlorophenol (15 mg, 0.9×10^{-4} mol) using Pd-PFA in supercritical CO_2 at 50 °C and 100 atm. ■: 2,4-dichlorophenol, ▲: cyclohexanone, □: cyclohexanol, Δ: cyclohexane, ○: phenol.

Supporting information



NMR spectrum of products after hydrodechlorination of chlorobenzene using Pd-PFA for 60 minutes at 50 °C. The chlorobenzene peaks around 7.1 – 7.4 ppm disappeared, and two peaks due to benzene and cyclohexane appeared at 7.3 ppm and 1.4 ppm, respectively.



NMR spectrum of products after hydrodechlorination of 4-chlorobiphenyl using Pd-PFA for 30 minutes at 80 °C (top), standard NMR spectrum of 4-chlorobiphenyl (bottom). The reagent contained a small amount of H_2O as impurity and an unknown peak at 1.3 ppm.

Swelled Plastics in Supercritical CO₂ as Media for Stabilization of Metal Nanoparticles and for Catalytic Hydrogenation

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Swelled plastics in supercritical carbon dioxide provide unique environments for stabilizing palladium and rhodium nanoparticles and for catalytic hydrogenation. Complete hydrogenation of benzene to cyclohexane can be achieved in 10 minutes using the plastic stabilized Rh nanoparticles at 50 °C in supercritical CO₂. High efficiency, reusability, and rapid separation of products are some advantages of the plastic stabilized metal nanoparticles for catalytic hydrogenation in supercritical CO₂.

There has been much interest recently in synthesizing nanometer-sized metal particles because of their potential applications as new catalysts for organic reactions¹⁻³. The effect of size of metal nanoparticles on catalytic activities is one of the interesting aspects of the current research in this area⁴. However, nanometer-sized metal particles are unstable and tend to agglomerate without a suitable support. Different stabilizing approaches for nanoparticles have been reported in the literature including the use of chemical stabilizers³, dendrimers², polymers⁵ and microemulsions⁶.

In this paper, we report a novel approach of catalytic hydrogenation in supercritical CO₂ using palladium and rhodium nanoparticles stabilized in plastics. Since plastics swell in supercritical CO₂^{7,8}, metal precursors dissolved in the fluid phase can penetrate into plastic structures. After hydrogen reduction of the metal precursors, the resulting metals are trapped as nanometer-sized particles and stabilized in the plastic structures. During catalytic hydrogenation, starting materials dissolved in CO₂ can penetrate into the swelled plastic structures and diffuse into the interior of the plastic containing metal nanoparticle for catalytic hydrogenation to take place effectively. Because the hydrodynamic diameters of metal nanoparticle trapped in the plastic are much larger than that of starting materials (such as benzene and phenol), the plastic structures allow the reactants to diffuse into the interior but forbid metal nanoparticles to diffuse and to agglomerate. Therefore, not only the metal nanoparticles exist on the surface of the plastic but also present in the interior of the plastic are available for catalysis in supercritical CO₂. Consequently, the amount of metal nanoparticles per volume of the supporting plastic material can be extremely high compared with those of conventional active carbon and alumina supported metal catalysts. Thus, the plastic stabilized Pd and Rh nanoparticles can be used repeatedly without losing their catalytic capabilities. After reaction, the products of the catalytic hydrogenation diffuse away from the plastic structure. Finally the products can be easily separated from the plastic catalysts by rapid expansion of CO₂.

The plastic supported palladium and rhodium nanoparticles were prepared by hydrogen reduction of Pd(II) hexafluoroacetylacetonate [Pd(hfa)₂] and Rh(III) acetylacetonate [Rh(acac)₃] in supercritical CO₂. Watkins and McCarthy previously reported that nanometer-sized platinum particles could be uniformly deposited into poly(4-methyl-1-pentene) and

poly(tetrafluoroethylene) in supercritical CO₂ by hydrogen reduction of a platinum precursor⁹. In our experiments, a 50 mL high-pressure stainless flat-bottom cell was used for the synthesis of the metal nanoparticles. High density polyethylene (HDPE) granules (3 mm diameter) and fluoropolymer (PFA) tube (6 mm diameter) obtained from Aldrich were used as supporting plastics. The PFA tubing was sliced to rings with 1 mm width. The plastic materials were placed in a 50 mL high-pressure cell together with 250 mg of the metal precursor [Pd(hfa)₂ or Rh(acac)₃]. The 50 mL cell was then pressurized by 100 atm CO₂ to dissolve the Pd or Rh precursor in supercritical CO₂. Hydrogen gas (10 atm) was introduced into a separate injection vessel (10 mL volume) followed by pressurizing the injection vessel with 200 atm CO₂. By opening an interconnecting valve between the 50 mL high-pressure cell and the 10 mL injection vessel, hydrogen was injected into the 50 mL high pressure cell with the aid of the pressure difference between the two cells. The hydrogen reduction of Pd(hfa)₂ was performed at 200 atm and 50 ± 5 °C. After about 2 hours, Pd was successfully deposited into HDPE granules or PFA rings. The yellowish color caused by Pd(hfa)₂ became dark gray due to Pd metal particle formation as seen in Fig. 1a. A piece of the PFA with Pd nanoparticles was cut in half for observation. The whole cross section (width 1 mm) was also dark gray in color indicating that the Pd precursor penetrated deep into the whole PFA ring in supercritical CO₂ and deposited uniformly in the plastic as metal nanoparticles. Fig. 1b shows a TEM micrograph of the Pd nanoparticles deposited in HDPE. The method for TEM sample preparation was identical to that reported in the literature⁹. From the TEM micrograph, the size distribution of the metal nanoparticles was estimated to vary from 2 to 10 nm with the largest fraction in the range of 4–5 nm in diameter.

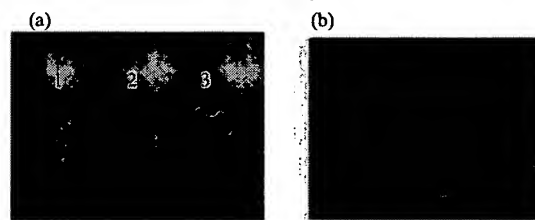


















Fig. 1 (a) Optical image of HDPE, 1) original, 2) with Pd(hfa)₂, 3) with Pd nanoparticles (b) TEM micrographs of Pd nanoparticles deposited in HDPE; scale = 50 nm.

In the synthesis of Rh nanoparticles, 3.5 mL chloroform were added to enhance the solubility of Rh(acac)₃ in supercritical CO₂. In addition, 10 mg of Pd(hfa)₂ were also added as a catalyst for hydrogen reduction of Rh(acac)₃. The Rh nanoparticle depositions in HDPE granule and PFA ring were performed at 110 °C and 150 °C, respectively. The plastic supported metal nanoparticles are very stable in air. No obvious agglomeration of the metal nanoparticles in the plastic materials was observed even after 3 months of storage in our laboratory based on TEM micrographs.

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See <http://www.rsc.org/suppdata/cc/b0/b000000a/>

It should be noted that newly prepared plastic stabilized Pd and Rh catalysts must be washed thoroughly in supercritical CO₂ to remove possible byproducts produced from the reduction process. We recommend washing of the plastic catalysts with neat supercritical CO₂ at 100 atm and 50 °C repeatedly until the byproducts (hexafluoroacetylacetone from Pd(hfa)₂ and acetylacetone from Rh(acac)₃) are no longer detectable from the trapped solution. Hydrogenation of olefins, arenes and nitro compounds were studied using the plastic supported Pd or Rh nanoparticles prepared by the procedure given above. The plastic catalyst and the starting material were placed in a 10 ml high-pressure stainless cell. The stainless cell was heated to a desired reaction temperature (e.g. 50 °C) in an oven. Hydrogen gas was flowed through the whole system to purge air and then was pressurized to 10 atm. Finally the reactor was pressurized by 100 atm of CO₂ to allow the starting material to dissolve in the CO₂ phase and for the hydrogenation reaction to occur. After a reaction time of 10 - 60 minutes, the reaction products were collected in a CDCl₃ solution by the RESS technique for NMR measurements using a 300 MHz NMR spectrometer (BRUKER AMX 300). The results of hydrogenation of arenes using the plastic supported Pd or Rh nanoparticles as catalysts are summarized in Table 1.

Table 1 Hydrogenation of arenes using the plastic supported metal nanoparticles.

Metal	Polymer	Starting Material	Temperature (°C)	Time	Products (Conversion)
Pd	HDPE	 20 mg	50	15 min	 (~100 %)
Rh	PFA	 15 µl	50	10 min	 (99 %)
Pd	PFA	 15 µl	50	60 min	 (86 %)
Pd	HDPE	 15 mg	50	60 min	 (79%)  (6%)
Pd	PFA	 15 mg	50	50 min	 (82 %)  (39%)
Rh	PFA	 15 mg	50	20 min	 (60 %)  (33 %)  (5 %)

Hydrogenation of arenes using conventional Group VIII metal catalysts usually requires high temperatures and/or additives to facilitate the reaction. For example, in industrial processes, benzene is reduced to cyclohexane at high temperatures (2.5 MPa, 220 - 397 °C) over either supported platinum or nickel in quantitative yield¹⁰. Using the plastic stabilized Pd nanoparticles as catalysts (in HDPE granule or in PFA ring), the hydrogenation of arenes proceeds rapidly even at 50 °C. Hydrogenation of naphthalene to form tetralin was completed within 15 minutes under our experimental conditions. In order to examine the recyclability of the plastic supported metal nanoparticles, the hydrogenation of naphthalene using the HDPE supported Pd nanoparticle catalyst was repeated 10 times under the same experimental conditions. The conversion of naphthalene to tetralin was always >99 % and did not show an obvious decrease in hydrogenation efficiency. The fine structures of the plastic are effective for preventing diffusion and agglomeration of the

nanoparticles in the plastic structures. On the other hand, the arenes can diffuse smoothly in the swelled polymer structures and can contact with nanoparticles, because of the extremely small hydrodynamic diameter compared with that of nanoparticles. The plastic stabilized Rh nanoparticles are more effective than the Pd nanoparticles for catalytic hydrogenation of arenes. The hydrogenation of benzene to cyclohexane using the PFA stabilized Rh nanoparticles was almost completed (99%) within 10 minutes at 50 °C with 10 atm H₂ and 100 atm CO₂. Using PFA stabilized Pd nanoparticles under the same reaction conditions, conversion of benzene to cyclohexane was 86% after 60 min. Fig. 2 shows a typical NMR spectrum of the reaction products found in the trap solution after hydrogenation of benzene using the Rh catalyst in supercritical CO₂. The only major peaks found in the NMR spectrum are cyclohexane (1.4 ppm) and chloroform from CDCl₃ (7.2 ppm). Two very small peaks at 1.5 ppm and 7.3 ppm are due to H₂O and the starting material benzene (< 1%), respectively. This result clearly shows that the separation of the product from the plastic catalyst can be achieved by rapid exsipation of CO₂. The Rh nanoparticles are also more effective than Pd for hydrogenation of phenol to cyclohexanone (major) and cyclohexanol (minor).

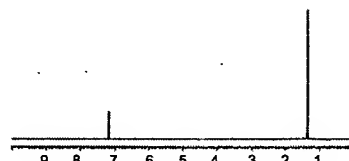


Fig. 2 NMR spectrum of hydrogenation of benzene using the Rh nanoparticles

The hydrogenation of olefin and nitro compounds were also tested using PFA supported Pd nanoparticles. 4-methoxy cinnamic acid (15 mg) was converted to 4-methoxy hydrocinnamic acid (>98%) in 5 minutes at 50 °C with 10 atm of H₂ and 100 atm of CO₂. Nitrobenzene (15 µL) was converted to aniline (>98%) with minor products (<2%) cyclohexyl amine and cyclohexane in 5 minutes under the same conditions in supercritical CO₂.

Because of their stability, recyclability, easy handling and separation of products, the plastic supported Pd and Rh nanoparticles may have a wide range of applications in chemical synthesis and manufacturing processes. The technique can be applied to other catalytic metals and different plastics. Since various forms of high temperature plastics such as polyimide, polytetrafluoroethylene and polybenzimidazole are commercially available, the plastic supported metal nanoparticles may be used for high temperature catalytic reactions.

This work was supported by Idaho NSF-EPSCoR and ARO-DEPSCoR programs.

Notes and references

- (1) H. Ohde, C. M. Wai, H. Kim, J. Kim, M. Ohde, *J. Am. Chem. Soc.* 2002, 124, 4540.
- (2) Y. Niu, L. K. Yeung, R. M. Crooks, *J. Am. Chem. Soc.* 2001, 123, 6840.
- (3) A. Henglein, B. G. Ershov, M. Malow, *J. Phys. Chem.* 1995, 99, 14129.
- (4) T. K. Sau, A. Pal, T. Pal, *J. Phys. Chem. B* 2001, 105, 9266.
- (5) J. Dai, M. L. Bruening, *Nano.Lett.* 2002, 2, 497.
- (6) D. M. de Jesus, M. Spiro, *Langmuir* 2000, 16, 4896.
- (7) J. Shim, K. P. Johnston, *AIChE J.* 1991, 37, 607.
- (8) R. G. Wissinger, M. E. Paulaitis, *J. Polym. Sci. Polym. Phys. Ed.*, 1987, 25, 2497.
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Single Column Figure/Scheme

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Fig./Scheme XX Caption.

Double Column Figure/Scheme

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Fig./Scheme XX Caption.

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Double Column Uncaptioned Graphic

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Numbered Equation

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Single Column Table

Table XX Caption

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^a Footnote text.

Double Column Table

Table XX Caption

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^a Footnote text.

Swelled Plastics in Supercritical CO₂ as Media for Stabilization of Metal Nanoparticles and for Catalytic Hydrogenation

Hiroyuki Ohde, Mariko Ohde, Chien M. Wai

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Tel: (+1)208-885-6787; E-mail: cwai@uidaho.edu

*This submission was created using the RSC ChemComm Template (DO NOT DELETE THIS TEXT)
(LINE INCLUDED FOR SPACING ONLY - DO NOT DELETE THIS TEXT)*

Swelled plastics in supercritical carbon dioxide provide unique environments for stabilizing palladium and rhodium nanoparticles and for catalytic hydrogenation. Complete hydrogenation of benzene to cyclohexane can be achieved in 10 minutes using the plastic stabilized Rh nanoparticles at 50 °C in supercritical CO₂. High efficiency, reusability, and rapid separation of products are some advantages of the plastic stabilized metal nanoparticles for catalytic hydrogenation in supercritical CO₂.

There has been much interest recently in synthesizing nanometer-sized metal particles because of their potential applications as new catalysts for organic reactions¹⁻³. The effect of size of metal nanoparticles on catalytic activities is one of the interesting aspects of the current research in this area⁴. However, nanometer-sized metal particles are unstable and tend to agglomerate without a suitable support. Different stabilizing approaches for nanoparticles have been reported in the literature including the use of chemical stabilizers³, dendrimers², polymers⁵ and microemulsions⁶.

In this paper, we report a novel approach of catalytic hydrogenation in supercritical CO₂ using palladium and rhodium nanoparticles stabilized in plastics. Since plastics swell in supercritical CO₂^{7,8}, metal precursors dissolved in the fluid phase can penetrate into plastic structures. After hydrogen reduction of the metal precursors, the resulting metals are trapped as nanometer-sized particles and stabilized in the plastic structures. During catalytic hydrogenation, starting materials dissolved in CO₂ can penetrate into the swelled plastic structures and diffuse into the interior of the plastic containing metal nanoparticle for catalytic hydrogenation to take place effectively. Because the hydrodynamic diameters of metal nanoparticle trapped in the plastic are much larger than that of starting materials (such as benzene and phenol), the plastic structures allow the reactants to diffuse into the interior but forbid metal nanoparticles to diffuse and to agglomerate. Therefore, not only the metal nanoparticles exist on the surface of the plastic but also present in the interior of the plastic are available for catalysis in supercritical CO₂. Consequently, the amount of metal nanoparticles per volume of the supporting plastic material can be extremely high compared with those of conventional active carbon and alumina supported metal catalysts. Thus, the plastic stabilized Pd and Rh nanoparticles can be used repeatedly without losing their catalytic capabilities. After reaction, the products of the catalytic hydrogenation diffuse away from the plastic structure. Finally the products can be easily separated from the plastic catalysts by rapid expansion of CO₂.

The plastic supported palladium and rhodium nanoparticles were prepared by hydrogen reduction of Pd(II) hexafluoroacetylacetonate [Pd(hfa)₂] and Rh(III) acetylacetonate [Rh(acac)₃] in supercritical CO₂. Watkins and McCarthy previously reported that nanometer-sized platinum particles could be uniformly deposited into poly(4-methyl-1-pentene) and

poly(tetrafluoroethylene) in supercritical CO₂ by hydrogen reduction of a platinum precursor⁹. In our experiments, a 50 mL high-pressure stainless flat-bottom cell was used for the synthesis of the metal nanoparticles. High density polyethylene (HDPE) granules (3 mm diameter) and fluoropolymer (PFA) tube (6 mm diameter) obtained from Aldrich were used as supporting plastics. The PFA tubing was sliced to rings with 1 mm width. The plastic materials were placed in a 50 mL high-pressure cell together with 250 mg of the metal precursor [Pd(hfa)₂ or Rh(acac)₃]. The 50 mL cell was then pressurized by 100 atm CO₂ to dissolve the Pd or Rh precursor in supercritical CO₂. Hydrogen gas (10 atm) was introduced into a separate injection vessel (10 mL volume) followed by pressurizing the injection vessel with 200 atm CO₂. By opening an interconnecting valve between the 50 mL high-pressure cell and the 10 mL injection vessel, hydrogen was injected into the 50 mL high pressure cell with the aid of the pressure difference between the two cells. The hydrogen reduction of Pd(hfa)₂ was performed at 200 atm and 50 ± 5 °C. After about 2 hours, Pd was successfully deposited into HDPE granules or PFA rings. The yellowish color caused by Pd(hfa)₂ became dark gray due to Pd metal particle formation as seen in Fig. 1a. A piece of the PFA with Pd nanoparticles was cut in half for observation. The whole cross section (width 1 mm) was also dark gray in color indicating that the Pd precursor penetrated deep into the whole PFA ring in supercritical CO₂ and deposited uniformly in the plastic as metal nanoparticles. Fig. 1b shows a TEM micrograph of the Pd nanoparticles deposited in HDPE. The method for TEM sample preparation was identical to that reported in the literature⁹. From the TEM micrograph, the size distribution of the metal nanoparticles was estimated to vary from 2 to 10 nm with the largest fraction in the range of 4–5 nm in diameter.

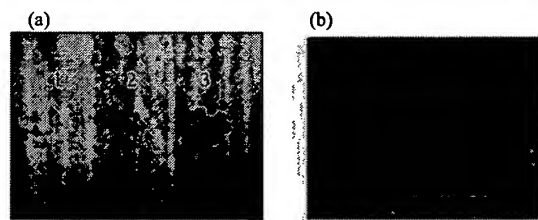


















Fig. 1 (a) Optical image of HDPE, 1) original, 2) with Pd(hfa)₂, 3) with Pd nanoparticles (b) TEM micrographs of Pd nanoparticles deposited in HDPE; scale = 50 nm.

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It should be noted that newly prepared plastic stabilized Pd and Rh catalysts must be washed thoroughly in supercritical CO₂ to remove possible byproducts produced from the reduction process. We recommend washing of the plastic catalysts with neat supercritical CO₂ at 100 atm and 50 °C repeatedly until the byproducts (hexafluoroacetylacetone from Pd(hfa)₂ and acetylacetone from Rh(acac)₃) are no longer detectable from the trapped solution. Hydrogenation of olefins, arenes and nitro compounds were studied using the plastic supported Pd or Rh nanoparticles prepared by the procedure given above. The plastic catalyst and the starting material were placed in a 10 ml high-pressure stainless cell. The stainless cell was heated to a desired reaction temperature (e.g. 50 °C) in an oven. Hydrogen gas was flowed through the whole system to purge air and then was pressurized to 10 atm. Finally the reactor was pressurized by 100 atm of CO₂ to allow the starting material to dissolve in the CO₂ phase and for the hydrogenation reaction to occur. After a reaction time of 10 - 60 minutes, the reaction products were collected in a CDCl₃ solution by the RESS technique for NMR measurements using a 300 MHz NMR spectrometer (BRUKER AMX 300). The results of hydrogenation of arenes using the plastic supported Pd or Rh nanoparticles as catalysts are summarized in Table 1.

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Metal	Polymer	Starting Material	Temperature (°C)	Time	Products (Conversion)
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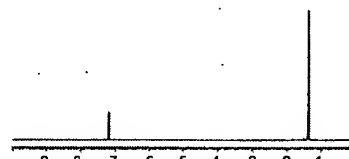


Fig. 2 NMR spectrum of hydrogenation of benzene using the Rh nanoparticles

The hydrogenation of olefin and nitro compounds were also tested using PFA supported Pd nanoparticles. 4-methoxy cinnamic acid (15 mg) was converted to 4-methoxy hydrocinnamic acid (>98%) in 5 minutes at 50 °C with 10 atm of H₂ and 100 atm of CO₂. Nitrobenzene (15 µL) was converted to aniline (>98%) with minor products (<2%) cyclohexyl amine and cyclohexane in 5 minutes under the same conditions in supercritical CO₂.

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Notes and references

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- (6) D. M. de Jesus, M. Spiro, *Langmuir* 2000, 16, 4896.
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Single Column Figure/Scheme

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Fig./Scheme XX Caption.

Double Column Figure/Scheme

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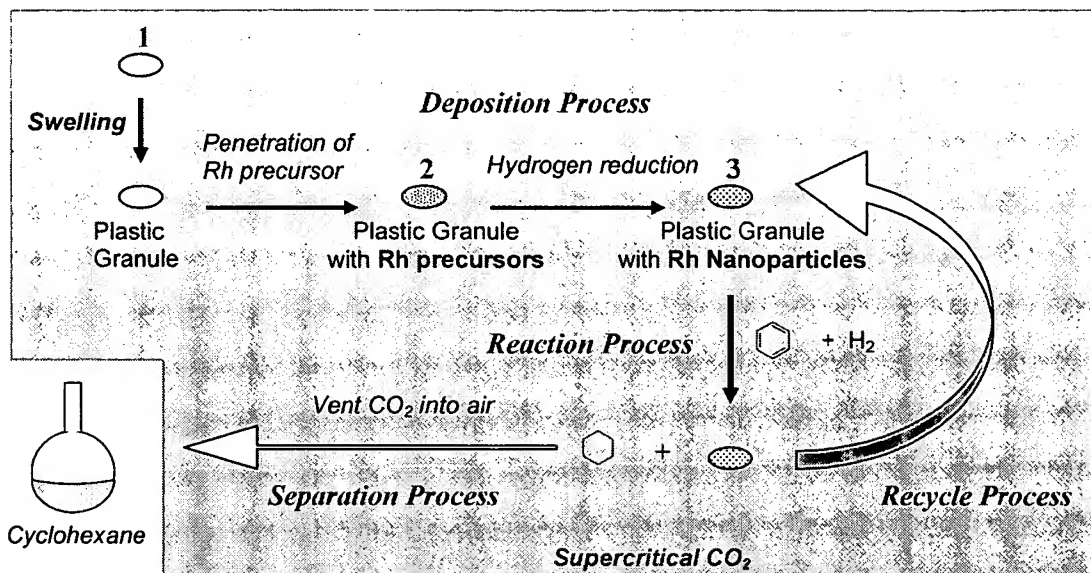
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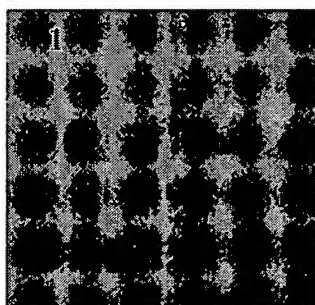
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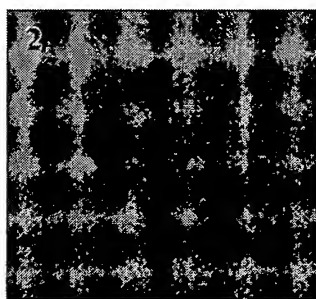
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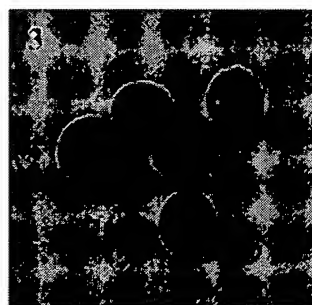
Catalytic hydrogenation of benzene using Rh nanoparticles stabilized in plastic granules



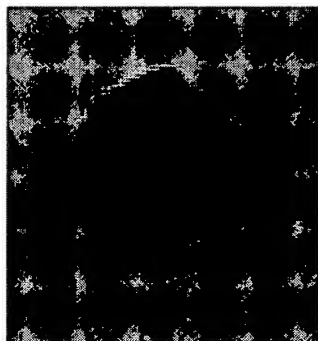
Plastic Granule



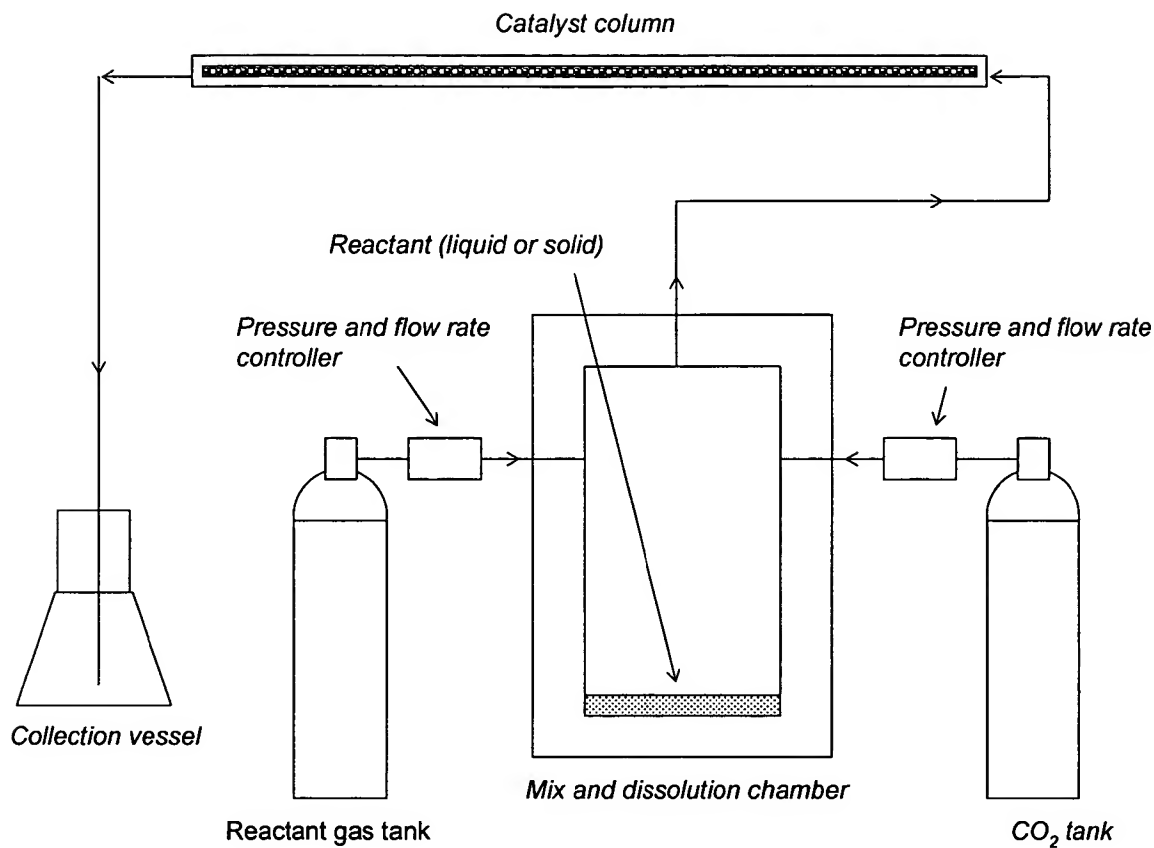
Plastic Granule with Rh precursor



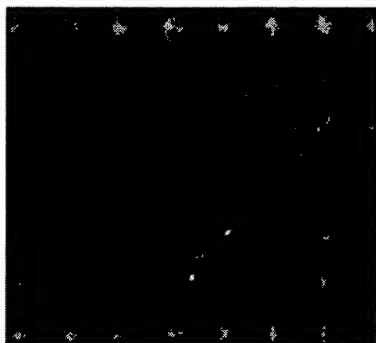
Plastic Granule with Rh nanoparticles



A cut surface of the plastic granule was also black in color indicative of uniform dispersion of Rh nanoparticles inside the plastic.



Schematic diagram of CO₂-based catalysis system with a catalyst column prepared by packing a tubular stainless vessel with plastic stabilized metal particles.



Plastic granules with Ag nanoparticles were yellow in color originated from the surface plasmon resonance absorption. The coloration was not changed for such a long period of time as years.

DISCLOSURE OF INVENTION OR COPYRIGHTABLE WORK

DISCLOSURE OF INVENTION OR COPYRIGHTABLE WORK

I. DESCRIPTIVE

1. Title of Invention

Polymer Stabilized Metal, Alloy and Semiconductor Nanoparticles for Catalytic Reactions in Supercritical Carbon Dioxide

2. Brief description. Is the invention a new process, composition of matter, a device or one or more products? A new use of, or an improvement to, an existing product or process?

This invention is a new method for a wide range of catalytic reactions in supercritical fluid carbon dioxide using nanometer-sized metal (include metal oxide), alloy and semiconductor particles stabilized in polymer materials as catalysts. Because polymers swell in supercritical carbon dioxide due to dissolution of CO₂ in polymer matrix, CO₂-soluble metal, alloy and semiconductor precursors can penetrate deep inside the polymer matrix. By chemical reactions of these precursors penetrated in the polymer, high concentrations of the metal, alloy and semiconductor materials were uniformly trapped as nanometer-sized particles in the polymer matrix without aggregation. These nanoparticles embedded in polymer materials are effective catalysts for a wide range of chemical reactions (e.g. hydrogenation, dehydrogenation, hydrolysis, oxidation, dechlorination, Heck reaction and photochemical reactions) conducted in supercritical fluid carbon dioxide. Since the polymer swells again during catalytic reactions, reactants dissolved in the fluid phase can penetrate inside the polymer matrix in contact with all metal, alloy and semiconductor nanoparticles deposited inside the polymer materials. Thus, the catalytic reactions are not limited to the nanoparticles deposited on the surface of the polymer materials, and high catalytic efficiencies can be achieved. The nanoparticles in polymer materials can be repeatedly used without losing catalytic capability according to our experiments. The stabilizing polymer materials may be plastics, fabrics and natural polymers, which enable us to build a sophisticated and clean, CO₂ based-catalysis system. For example, a long tubular stainless vessel can be packed with small plastic granules contain metal, alloy and semiconductor nanoparticles. The tubular stainless vessel works as a recyclable catalyst column. By flowing reactants dissolved in supercritical CO₂ through the catalyst column, the products can be collected from the outlet of the column continuously.

3. From the description, pick out and expand on novel and unusual features. How does the invention differ from present technology? What problems does it solve, or what advantages does it possess?

Supercritical carbon dioxide offers several advantages over conventional organic solvents for conducting catalytic reactions. One advantage is based on the fact that various gases such as hydrogen and oxygen are miscible with CO₂, thus high concentrations of those gases can be introduced in the supercritical CO₂ phase for a wide range of hydrogenation and oxidation

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reactions. Easy separation of products and minimum liquid waste generation are other advantages of conducting chemical reactions in supercritical carbon dioxide. Metal, alloy and semiconductor particles with nanometer sizes are effective catalysts because of the large surface area per volume and the high ratio of surface atoms to bulk atoms. Surface atoms have a higher catalytic activity than bulk atoms. Metal, alloy and semiconductor nanoparticles are usually very reactive and tend to aggregate without a stabilizing support. Fine structures in polymer matrix forbid those nanoparticles to aggregate and keep them reactive for a long period of time probable up to years. Therefore, in a combination of polymer stabilized metal, alloy and semiconductor nanoparticles as catalysts with supercritical carbon dioxide as a solvent, highly efficient catalytic reactions can be achieved. Commercially available heterogeneous catalysts usually have metal particles only on the surface of supporting materials. Also the supporting material such as carbon or alumina do not swell in supercritical carbon dioxide, thus conventional heterogeneous catalysts have limited catalytic capability. Moreover, these conventional catalysts are often moisture sensitive and/or irritant, because the fine particles are exposed to air, and the particles aggregate or fall off the catalyst surface easily by repeated use.

4. If not indicated previously, what are possible uses for the invention? In addition to immediate applications, are there other uses that might be realized in the future?

This new catalyst system can be used for some catalytic reactions in supercritical CO₂. For example, effective conversions of benzene and naphthalene to cyclohexane and decalin, respectively, using the plastic stabilized rhodium nanoparticles can be achieved at a low temperature as 50 °C, these aromatic compounds may be organic hydrogen storage systems for fuel-cell applications. Converting benzene to cyclohexane is also important for preparation of low-aromatic diesel fuels. The new catalyst system can also remove chlorine from chlorocompounds by hydrodechlorination. For example, chlorobenzene can be converted to cyclohexane and HCl at 50 °C thus converting a toxic chlorinated aromatic compound to a harmless one. This method can also be applied to converting polychlorinated biphenyls (PCBs) to dicyclohexyl for environmental remediation purposes. Semiconductor nanoparticles may be used for photochemical reactions using optically transparent polymer materials as stabilizing polymer.

Does the invention possess disadvantages or limitations? Can they be overcome? How?

The methods described in this invention are probably limited for supercritical fluid processes that usually are carried out in pressurized systems and require use of stainless steel containers. The polymer stabilized metal, alloy and semiconductor nanoparticles may be used for catalytic reactions in vapor phase, because gas molecules can slowly penetrate into polymer matrix without swelling of the polymer structure.

5. Enclose sketches, drawings, photographs and other materials that help illustrate the description. (Rough artwork, flow sheets, Polaroid photographs and penciled graphs are satisfactory as long as they tell a clear and understandable story.)

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II. OTHER PERTINENT DATA

1. Has the invention been described in specific detail or in a general way in a publication? ("Publication" for this purpose includes abstracts of talks, news stories, student theses, etc., as well as published scientific papers.) Has the invention been described orally at a meeting? Please provide exact details including dates and copies of any publications.

Not yet.

2. Is a publication or oral disclosure descriptive of the invention planned within the next year? Give date (estimate if unknown) and attach copies of any existing manuscripts, preprints or abstracts. (Please continue to keep IRF informed of any disclosure dates.)

A manuscript regarding catalytic hydrogenation of olefins and arenes has been submitted for publication but has not been accepted for publication, yet.

3. Has the invention been tested experimentally? Are experimental data available?

Yes.

4. Are there known inventions by other research workers that are related to this one? Please describe, including information on relevant patents and publications if available.

No. Not to our knowledge.

5. Was the work that led to the invention sponsored? If yes, attach copy of contract or agreement if possible, and fill in the appropriate blanks below.

The work was supported by the Idaho NSF-EPSCoR and Army Research Office

- a. Title of government agency - NSF, ARO

Contract or grant no. Idaho NSF-EPSCoR (EPS-0132626)
Army DEPSCoR DAAD19-01-1-0458

- b. Name of industrial company

- c. Name of university sponsor

- d. Other sponsor(s)

6. Has the invention been disclosed to industry representatives? Has any commercial interest been shown in it? Name companies and specific individuals and their titles.

No

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7. Do you know of other firms that might be particularly interested in the invention?

No.

8. Complete name(s), home and University addresses, title(s) and citizenship of inventor(s). This information must be accurately completed, as home address and citizenship will be needed for use in the U.S. Patent and Trademark Office.

a. Wai Chien M USA
 (Last) (First) (MI) (Cit)

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DISCLOSURE OF INVENTION OR COPYRIGHTABLE WORK

9. Title of Invention (same as Part I, Section 1)

Polymer Stabilized Metal and Semiconductor Nanoparticles for Catalytic Reactions in Supercritical Carbon Dioxide

Signature(s) of inventor(s), with date Witness to Signatures:

a.

(date)

b.

(date)

10. Read and understood by:

(date)

(Print Name)

Use the space below and additional sheets to elaborate on answers to questions and to provide experimental data accounting for your disclosure statements.

Are your notebook records available for review? Are they properly signed, witnessed, and dated?

Yes.

DISCLOSURE OF INVENTION OR COPYRIGHTABLE WORK

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DISCLOSURE OF INVENTION OR COPYRIGHTABLE WORK

I. DESCRIPTIVE

1. Title of Invention

Making metal films on polymer surfaces in supercritical fluids

2. Brief description. Is the invention a new process, composition of matter, a device or one or more products? A new use of, or an improvement to, an existing product or process?

The invention is a new process of making metal films on polymer surfaces done in a supercritical fluid such as supercritical carbon dioxide. The technique in principle can coat different metals on different polymer surfaces. Because of the penetration power of supercritical fluids, the metal films are formed deep into the surfaces and hence can not be removed by rubbing. Other surface coating techniques such as vapor deposition can not penetrate into the plastic surface like this proposed supercritical fluid deposition technique.

3. From the description, pick out and expand on novel and unusual features. How does the invention differ from present technology? What problems does it solve, or what advantages does it possess?

This novel method of making metal films on polymer surfaces uses a reducing agent, such as hydrogen, to cause reduction of an organometallic compound dissolved in a supercritical fluid such as supercritical carbon dioxide. The reduced metal is formed on the surface of a polymer as a thin film. Because supercritical carbon dioxide can penetrate into the polymer surface, the metal film is formed from the very surface to below the surface molecular layers. The depth of the metal film is perhaps in the order of tens of molecular layers. The film can not be removed by surface rubbing. The coated polymer should conduct current. Also the property of the polymer surface should be changed. These properties should have many applications in developing new materials and in electronics.

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4. If not indicated previously, what are possible uses for the invention? In addition to immediate applications, are there other uses that might be realized in the future?

For use in electronics, in conducting current and heat, in development of light reflecting low weight materials, making stronger and high temperature resisting polymers, etc.

5. Does the invention possess disadvantages or limitations? Can they be overcome? How?

The process of reduction of organometallic compound requires high temperature. For example, reduction of copper can be done by hydrogen reduction of copper hexafluoroacetylacetonate in supercritical carbon dioxide at 250 °C and pressure of several thousand psi. Only high temperature polymers such as polyimide, polyetheretherketone (PEEK), and Teflon can be coated with copper using this method. Coating other metals may require different temperature and pressure. Using different organometallic compounds should change the temperature and pressure of the reduction process. Other reducing agents may also be used to cause metal reduction of organometallic compounds in supercritical fluids.

6. Enclose sketches, drawings, photographs and other materials that help illustrate the description. (Rough artwork, flow sheets, Polaroid photographs and penciled graphs are satisfactory as long as they tell a clear and understandable story.)

DISCLOSURE OF INVENTION OR COPYRIGHTABLE WORK**II. OTHER PERTINENT DATA**

1. Has the invention been described in specific detail or in a general way in a publication? ("Publication" for this purpose includes abstracts of talks, news stories, student theses, etc., as well as published scientific papers.) Has the invention been described orally at a meeting? Please provide exact details including dates and copies of any publications.

No.

2. Is a publication or oral disclosure descriptive of the invention planned within the next year? Give date (estimate if unknown) and attach copies of any existing manuscripts, preprints or abstracts. (Please continue to keep IRF informed of any disclosure dates.)

No.

3. Has the invention been tested experimentally? Are experimental data available?

Yes. Data are available.

4. Are there known inventions by other research workers that are related to this one? Please describe, including information on relevant patents and publications if available.

Unknown.

5. Was the work that led to the invention sponsored? If yes, attach copy of contract or agreement if possible, and fill in the appropriate blanks below.

a. Title of government agency

Contract or grant no.

b. Name of industrial company

c. Name of university sponsor

d. Other sponsor(s) Micron Technology Inc.

6. Has the invention been disclosed to industry representatives? Has any commercial interest been shown in it? Name companies and specific individuals and their titles.

Discussed with Micron scientists in general terms. Micron is interested in this discovery.

DISCLOSURE OF INVENTION OR COPYRIGHTABLE WORK

Do you know of other firms that might be particularly interested in the invention?

No

7. Complete name(s), home and University addresses, title(s) and citizenship of inventor(s). This information must be accurately completed, as home address and citizenship will be needed for use in the U.S. Patent and Trademark Office.

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(Use additional page if necessary to list additional inventors)

Inventor to contact for additional information:

ChienWai

DISCLOSURE OF INVENTION OR COPYRIGHTABLE WORK**9. Title of Invention (same as Part I, Section 1)****Signature(s) of inventor(s), with date Witness to Signatures:**a. *Chien M. Dai*

(date)

b. *Id. Chde*

(date)

c.

(date)

10. Read and understood by:

(date)

(Print Name)

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